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(54) Abstract Title

Production of high octane hydrocarbons by the selective dimerization of isobutene

(57) High octane hydrocarbons are produced by reacting hydrocarbon cuts containing isobutene with an acid catalyst in the presence of an alkyl ether, preferably MTBE, and a primary alcohol, preferably methanol, such that the molar ratio of primary alcohol + alkyl ether/isobutene is more than 0.1 and the molar ratio of primary alcohol/isobutene is less than 0.2. The starting mixture is introduced to a first reactor (A) and bottoms products are sent to a separator (B) from which the head is sent to a second reactor (D). Combined bottoms product from separators (B) and (E) are sent to a third separator (C) to yield bottoms products (9) comprising mainly dimerized isobutene. Alkyl ethers from the head of third separator (C) are recycled (8). Alcohol may optionally be removed by an absorption unit (F) and recycled (14).

FIG. 1

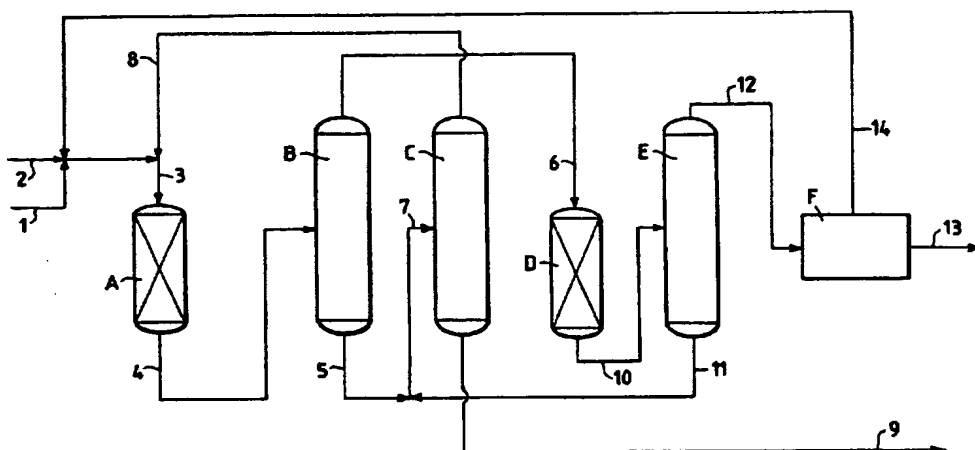
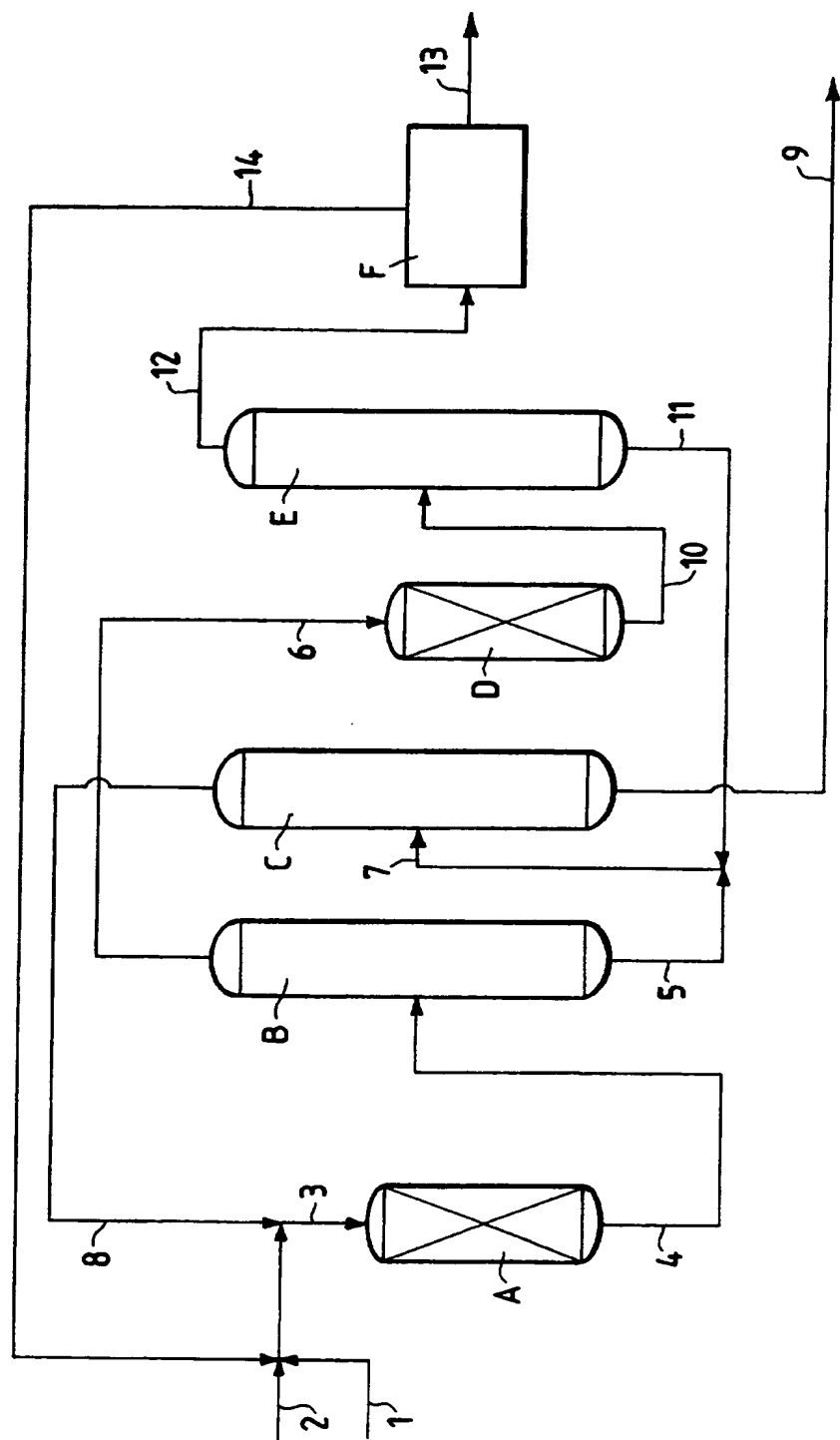


FIG. 1



PROCESS FOR THE PRODUCTION OF HYDROCARBONS WITH A HIGH
OCTANE NUMBER BY THE SELECTIVE DIMERIZATION OF ISOBUTENE.
NE.

The present invention relates to a process for the
5 production of hydrocarbons with a high octane number,
obtained by the selective dimerization reaction of
isobutene contained in hydrocarbon cuts and to a lesser
extent of possible linear butenes, in the presence of
moderate quantities of primary alcohols and alkyl
10 ethers, which favour the production of higher selecti-
vities on the part of the catalyst. The mixture ob-
tained can then be hydrogenated with the conventional
methods to obtain a product with a further improvement
in the octane characteristics.

15 For reasons of an environmental nature the compo-
sition of fuels is being reformulated; the "Clean Air
Act Amendments" (CAAA) in the United States are provid-
ing general regulations which will probably also be
adopted with a few variations by other countries in the

near future.

In short the general tendency is towards the production of fuels which burn better and have fewer evaporative emissions. The main measures for reaching this objective are the following (for more specific details see for example: G.H. Unzelman, Fuel Reformulation, 31(2), (1993), 41 and D. Sanfilippo, F. Ancillotti, M. Marchionna, Chim. & Ind., 76, (1994), 32 and references contained therein):

- 10 - oxygenated compounds will have an ever increasing role as fuel components;
- the content of aromatic compounds will be greatly reduced, especially in benzene;
- there will be a reduction in the volatility of fuels
- 15 to minimize evaporative losses;
- the content of light olefins, photochemically reactive and precursors responsible for the formation of atmospheric ozone, will be reduced;
- both the sulfur content and final boiling point of
- 20 fuels will also be reduced.

All these measures therefore lead to the necessity of planning new processes which can positively contribute to fulfilling the above demands.

As well as oxygenated compounds to which the CAAA

25 have assigned a fundamental role in future reformulated

fuels both for raising the octane number and supplying oxygen, purely hydrocarbon products are also proving to be particularly attractive.

Among these the alkylate is particularly distinctive as it has a high octane number, a low volatility and is practically without olefins and aromatics. The alkylation process in liquid phase is a reaction between isoparaffinic hydrocarbons, such as for example, isobutane, and olefins, for example propylene, butenes, pentenes and relative mixtures, in the presence of an acid catalyst for the production of C₇-C₉ hydrocarbons with a high octane number to be used in fuels (see for example: A. Corma, A. Martinez, Catal. Rev.- Sci. Eng., 35, (1993), 483 and references contained therein).

The main problem of the alkylation process is due to the fact that with the increase in environmental regulations both traditional processes (with hydrofluoric acid and sulfuric acid) are having considerable difficulties which makes their future uncertain; the process with hydrofluoric acid owing to the toxicity of this acid, especially in populated areas, and that with sulfuric acid owing to the large production of acid mud and also to the highly corrosive power of the catalyst.

Alternative processes with solid acid catalysts

are in the process of being developed but their commercial applicability is still to be proved.

On the other hand a hydrocarbon product of this type is in ever-increasing demand owing to its octane characteristics (high Research Octane Number (RON) and Motor Octane Number (MON) and those relating to its boiling point (poor volatility but low final point) which place it in the category of compositions which are extremely interesting for obtaining fuels that are more compatible with present-day environmental demands.

In addition, hydrocarbon products with a high octane number such as those generated by the alkylation reaction also have a low sensitivity (difference between RON and MON) and it is known that ethers such as MTBE, ETBE, TAME, etc. favourably react to the reduced sensitivity of the fuel, increasing their already high octane number even more.

This means that there are many advantages in combining a saturated hydrocarbon product with a high octane number (such as alkylate) with ethers such as MTBE. In addition the joint presence of considerable quantities of the two products also allows the content of undesired components such as aromatics, olefins and sulfur to be considerably decreased, by dilution.

In refining, an alternative process for obtaining

products with similar characteristics to alkylate can be offered by the hydrogenation of the so-called "polymer" fuel.

The oligomerization process (often erroneously
5 called, in the field of refining, polymerization) was widely used in the years 1930-1940 to convert low-boiling C_3 - C_6 olefins into fuels. The process leads to the production of a fuel with a high octane number (RON about 97) but with a high sensitivity owing to the
10 purely olefinic nature of the product (for more specific details on the process see: J.H. Gary, G.E. Handwerk, "Petroleum Refining: Technology and Economics", 3rd Ed., M. Dekker, New York, (1994), 250).

Typical olefins which are oligomerized are mainly
15 propylene, which gives slightly higher dimers or oligomers depending on the process used, and isobutene which mainly gives dimers but always accompanied by large quantities of higher oligomers.

With particular respect to the oligomerization of
20 isobutene it is known that this reaction can be carried out in batch, in semicontinuous or in continuous, in both gas-solid phase and liquid phase, generally at temperatures of between 50 and 300°C and at atmospheric pressure or at such pressures as to maintain the
25 reagents in liquid phase, if deemed suitable.

Typical catalysts for the industrial oligomerization of isobutene are represented by phosphoric acid, generally supported on a solid (for example kieselguhr), or acid resins with cation exchange. The latter
5 allow blander conditions of both temperature and pressure to be used than with supported phosphoric acid (100°C and 1-2 Mpa vs 200-220°C and 3-10 MPa).

Other catalysts have also been claimed in literature, both liquid acids such as H_2SO_4 or sulfonic acid
10 derivatives, and solids such as for example silico-aluminas, mixed oxides, zeolites, fluorinated or chlorinated aluminas, etc.; on the other hand none of these catalysts has as yet enabled the setting up of an industrial process as in the case of supported phosphoric acid (F. Asinger, "Mono-olefins: Chemistry and
15 Technology", Pergamon Press, Oxford, pages 435-456) and in that of cationic resins (G. Scharfe, Hydrocarbon Proc., April 1973, 171).

From the product point of view, the main problem
20 of this process lies in the fact that in the oligomerization phase heavy oligomers such as trimers (selectivity of 15-30%) and tetramers (selectivity of 1-2%) of isobutene are produced in excessive percentages. Tetramers are completely outside the fuel fraction as
25 they are too high-boiling and therefore represent a

distinct loss in fuel yield; with respect to trimers (or their hydrogenated derivatives) it is desirable to strongly reduce their concentration as their boiling point (170-180°C) is on the limit of future specifications on the final point of reformulated fuels.

On the other hand the problem of minimizing the formation of higher oligomers to dimers with percentages of less than 10% is a problem which is typical of the oligomerization of isobutene, as is also specified in literature (C.T. O'Connor, M.Kojima, K.W. Schumann, Appl. Catal., 16 (1985), 193).

This level of heavy compounds is analogous to that of an alkylate and is still tolerated in the fuel pool.

From what has been said above, it is evident that there is a wide interest in obtaining a new dimerization process of isobutene which allows the synthesis of a higher quality product, by reaching greater selectivities.

It has now been surprisingly found that by carrying out the selective dimerization reaction of isobutene in the presence of moderate quantities of primary alcohols and alkyl ethers, the production of a fraction of oligomers is selectively obtained, particularly rich in dimers (>90%) and practically without tetramers and higher oligomers (<0.05%), containing small quantities

of dimer ethers.

The reaction product is then preferably hydrogenated to give a completely saturated end-product with a high octane number and low sensitivity. The hydrogenation can be carried out with the conventional methods as described for example in F. Asinger, "Mono-olefins: Chemistry and Technology", Pergamon Press, Oxford, page 455.

As an example, table I indicates the octane numbers and relative boiling points of some of the products obtained with the process of the present invention.

TABLE I

=====			
15	Product	RON	MON b.p. (°C)
	di-isobutenes	100	89 100-105
	iso-octane	100	100 99
	tri-isobutenes	100	89 175-185
	hydrogenated		
20	tri-isobutenes	101	102 170-180
=====			

The process of the present invention for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene, by selective dimerization with acid catalysts is charac-

terized in that the reaction is carried out in the presence of primary alcohols in such a quantity as to have in the feeding a molar ratio primary alcohols + alkyl ethers/isobutene of more than 0.1, preferably
5 between 0.1 and 0.7, and a ratio primary alcohol/isobutene of less than 0.2, preferably between 0.005 and 0.1.

It should also be pointed out that in the case of C₄ hydrocarbon streams also comprising linear olefins it
10 has been observed that at least a part of the latter can be converted by reaction with isobutene into a hydrocarbon product without threaten their octane number. It is also preferable to carry out an enriching treatment, by means of pre-isomerization, of the
15 internal linear olefins, which would benefit the total octane number of the mixture.

The process claimed herein can be applied to cuts containing isobutane, isobutene, n-butane and n-butenes.

20 Although a wide variety of sources is available for supplying these streams, the most common ones concern those deriving from dehydrogenation processes of iso-paraffins, from FCC units and streams coming from steam cracking.

25 When the streams from steam-cracking contain

diolefins in addition to the desired mono-olefins, it is necessary to eliminate them by the typical removal treatment (for example extractions or selective hydrogenations).

5 As well as the hydrocarbon components, the stream comprises as specified above, primary alcohol (in great molar defect with respect to the iso-olefin) and alkyl ether.

 The primary alcohol used can be selected from
10 primary alcohols containing from 1 to 6 carbon atoms: methanol and/or ethanol are preferred.

 The alkyl ether used can be selected from those containing from 5 to 10 carbon atoms: MTBE (methyl-ter-butyl ether), ETBE (ethyl-ter-butyl ether), MSBE
15 (methyl-sec-butyl ether), ESBE (ethyl-sec-butyl ether) or mixtures of these are preferred.

 The isobutene together with the hydrocarbon stream in which it is contained is sent with the primary alcohol and alkyl ether, in strong stoichiometric
20 defect, into contact with the acid catalyst where the dimerization takes place. The primary alcohol is almost completely converted under the reaction conditions to dimer ether.

 The presence of a constant level of primary
25 alcohol in the reactors is fundamental for obtaining

the desired high selectivities as it enables the use of a catalytic species with the correct activity.

The fact of operating with the correct catalytic activity makes the reaction much more controllable also
5 from a thermal point of view with a consequent improvement in the quality of the product.

The quantity of alkyl ether sent to the reactors is such that, depending on the operating conditions, it can be either further produced or partially decomposed:
10 in the latter case, as the decomposition process is of endothermal ether, a part of the heat developed in the dimerization reaction can be absorbed, thus further improving the temperature control in the reactor. In addition, the alcohol liberated by the decomposition of
15 the ether, as well as interacting with the catalyst, can react with the dimers and butenes present in the reactor.

The optimum level of the sum of primary alcohol and alkyl ether which must be present in the reaction
20 environment to obtain selectivities to dimers close to or higher than 90% by weight, depends on the composition of the hydrocarbon charge.

When the charge consists of C_4 hydrocarbon cuts containing isobutene in a quantity of between 10 and
25 30% by weight and n-butenes in a quantity of between 25

and 50% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.2 and 0.6.

When the charge consists of C_4 hydrocarbon cuts
5 containing isobutene in a quantity of between 30 and 60% by weight, n-butenes in a quantity of more than 30% by weight and C_4 paraffins in a quantity of less than 15% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol
10 + alkyl ether/isobutene of between 0.1 and 0.6.

When the charge consists of C_4 hydrocarbon cuts containing isobutene in a quantity of between 28 and 60% by weight, C_4 paraffins in a quantity of more than 30% by weight and n-butenes in a quantity of less than
15 10% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.3 and 0.6.

When the charge consists of C_4 hydrocarbon cuts containing isobutene in a percentage of more than 80%
20 by weight, it is advisable to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.5 and 0.7.

Table II indicates the average compositions of typical C_4 hydrocarbon fractions coming from different
25 sources (FCC, Steam Cracking, dehydrogenation of

isobutane, streams of isobutene with a high concentration).

TABLE II

Typical percentage compositions of C₄ streams

5	=====
	Steam cracking FCC Dehydrogen. Conc.isobutene
	Isobutene 30-46 10-25 45-55 >90
	n-butenes 35-60 25-50 <10
	C ₄ satur. 4-8 30-60 45-55 <10
10	=====

For charges different from those generally available in industrial practice, it can be observed that the addition of considerable quantities of linear olefins with respect to the charge compositions cited above, causes a slight increase in the selectivity to dimers and therefore a limited reduction in the lower limit of the molar ratio primary alcohol + alkyl ether/isobutene previously indicated. On the contrary, an increase in the content of saturated hydrocarbons causes a slight deterioration in the selectivity and therefore the value of the lower limit of the ratio is slightly increased.

A wide variety of acid catalysts can be used for this process, among these, for example, mineral acids such as sulfuric acid, BF₃, supported phosphoric acid,

suitably modified zeolites, heteropolyacids and sulfonated polymeric resins, for example Amberlyst 15 and Amberlyst 35, etc, can be mentioned. Among these catalysts the use of macrolattice sulfonated resins, 5 generally copolymers of styrene and benzene, is preferred; the characteristics of these resins are amply described in literature (see for example A. Mitschker, R.Wagner, P.M. Lange, "Heterogeneous Catalysis and Fine Chemicals", M. Guisnet ed., Elsevier, Amsterdam (1988), 10 61).

A wide range of operating conditions can be used for producing hydrocarbons with a high octane number in the desired selectivities by the process of the present invention. It is possible to operate in vapor phase or 15 in liquid-vapor phase but the operation conditions in liquid phase are preferred.

The process of the present invention can operate under both batch and continuous conditions, considering however that the latter are much more advantageous in 20 industrial practice. The reactor configuration selected can be optionally selected from fixed bed, tubular fixed bed, adiabatic, stirred and finally column reactor which also allows the separation of the products (a description on the general use of this technology is provided for example in : J.L. De Garmo, V.N. 25

Paruledar, V. Pinjala, Chem. Eng. Progr., March 1992, 43).

The range of process conditions, operating in liquid phase, comprises a wide variety of operating
5 conditions which are described hereunder.

The pressure is preferably superatmospheric to maintain the reagents in liquid phase, generally below 5 MPa, more preferably between 0.2-2.5 MPa. The reaction temperature is preferably between 30 and 120°C.
10 The feeding space velocities of the alcohol-hydrocarbon stream should preferably be less than 30 h⁻¹, more preferably between 1 and 15 h⁻¹.

The isobutene is mainly converted in the reaction zone, however also part of the n-olefins can be converted to useful product; for the most part, there are
15 no limits in the concentration of iso-olefin in the hydrocarbon fraction even if it is preferable to have concentrations of between 2 and 60%; there are no limits in the ratio between isobutene and linear
20 olefins. It should be observed that in the case of streams coming from the dehydrogenation of isobutane there are no significant concentrations of linear butenes in the charge.

The process of the present invention can be
25 carried out in particular by means of the following

basic steps:

- a) feeding to a dimerization reactor the hydrocarbon cut containing isobutene together with a stream consisting of primary alcohols and a stream
5 containing alkyl ethers;
- b) sending the product leaving the dimerization reactor to a fractionation column from whose head a stream is obtained containing non-reacted isobutene and small quantities of ethers and
10 alcohols and from the bottom of which a stream containing dimers and alkyl ethers is removed;
- c) sending the stream containing non-reacted isobutene to a second reactor to complete the conversion of isobutene;
- 15 d) sending the product leaving the second reactor to a second fractionation column from whose head a stream is obtained containing C₄ hydrocarbons and primary alcohols and from whose bottom a stream containing C₄ hydrocarbons, dimers and alkyl
20 ethers is removed;
- e) sending to a third fractionation column the bottom streams removed from the two fractionation columns obtaining the desired hydrocarbon product at the bottom and a stream containing alkyl ethers at the
25 head, which is recycled to the first reactor;

f) sending the stream leaving the head of the second fractionation column to a separation unit of the primary alcohols which are subsequently recycled to the first reactor.

5 A recommended process scheme is shown in the enclosed FIG.1 to provide a clearer illustration of the present invention.

The stream (1) containing isobutene, joined to the feeding of primary alcohol (2) (methanol), is sent to
10 a first reactor (A) in which the C_4 iso-olefin is selectively converted to dimers.

The effluent (4) from the reactor (A) is sent to a separation column (B) where a stream (6) is removed at the head, essentially containing non-converted
15 olefins, alkyl ether (MTBE) and alcohol (methanol) in such quantities as to satisfy the molar ratios specified above, whereas at the bottom a stream (5) is removed essentially containing dimers, oligomers, ethers of dimers and alkyl ether (MTBE).

20 This stream (5) is sent to a separation column (C) where a stream is removed at the head, essentially containing alkyl ether (MTBE) recycled to the reactor (A), whereas at the bottom the synthesis product is obtained essentially consisting of dimers and small
25 quantities of oligomers and ethers of dimers.

The stream (6) is fed to a second reactor (D) in which the isobutane present is selectively converted to dimers. The effluent (10) from the reactor (D) is separated in a column (E) from which a bottom stream
5 (11) is removed, essentially containing alkyl ether (MTBE) and dimers, which is sent, together with the stream (5), to the column (C).

Optionally, the stream (12) at the head can be treated to remove the alcohol (methanol) contained
10 therein in a unit (F) which can consist for example of an absorption system of the primary alcohol on molecular sieves or an extraction of the alcohol itself with water. In both cases the alcohol recovered can be sent (14) to the reaction, whereas the hydrocarbon stream
15 (13) can be used in subsequent operations.

An example is now provided for a better illustration of the invention without limiting its scope in any way.

Example 1

20 With reference to the diagram in the figure, a hydrocarbon stream containing 50% by weight of isobutene, of the type obtained by the dehydrogenation of isobutane, is converted in the presence of suitable quantities of methanol and MTBE into a hydrocarbon
25 product with a high octane number containing about 90%

by weight of di-isobutenes, the rest consisting of trimers of isobutenes and ethers of di-isobutenes.

Tables III and IV show with reference to the enclosed figure, the quantities of the various streams of the plant indicated in kg/h, % weight, kmol/h and % mol.

The reactors (A) and (D) operate at a temperature at the outlet of 70°C and 75°C respectively and both at an operating pressure of 2 MPa.

10 The molar ratio methanol+MTBE/isobutene is 0.375 in reactor (A) and 0.154 in reactor (B).

The corresponding molar ratios methanol/isobutene are 0.008 in reactor (A) and 0.017 in reactor (B).

15 The catalyst used is a commercial macroporous sulfonated resin of the type Amberlyst 35 produced by Rohm & Haas, Co.

CLAIMS

- 1) A process for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene, by selective dimerization with acid catalysts characterized in that the
5 dimerization reaction is carried out in the presence of primary alcohols and alkyl ethers in such a quantity as to have in the feeding a molar ratio primary alcohols + alkyl ethers/isobutene of
10 more than 0.1 and a molar ratio primary alcohols/isobutene of less than 0.2.
- 2) The process according to claim 1, operating, at a reaction temperature of between 30 and 120°C, at a pressure of less than 5 MPa and feeding space
15 velocities of less than 30 h⁻¹.
- 3) The process according to claim 1 wherein the molar ratio in the feeding of primary alcohols + alkyl ethers/isobutene is between 0.1 and 0.7.
- 4) The process according to claim 1 wherein the molar
20 ratio in the feeding of primary alcohols/isobutene is between 0.05 and 0.1.
- 5) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 10 and 30% by
25 weight and n-butenes in a quantity of between 25

and 50% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.2 and 0.6.

- 5 6) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 30 and 60% by weight and n-butenes in a quantity of more than 30% by weight and C₄ paraffins in a quantity of less than 15% by weight and the molar ratio
- 10 primary alcohols + alkyl ethers/isobutene is between 0.1 and 0.6.
- 7) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 30 and 60% by
- 15 weight and C₄ paraffins in a quantity of more than 30% by weight and n-butenes in a quantity of less than 10% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.3 and 0.6.
- 20 8) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in quantities of more than 80% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.5 and 0.7.
- 25 9) The process according to claim 1 wherein the space

velocities in the feeding are between 1 and 15 h⁻¹.

- 10) The process according to claim 1 wherein the primary alcohol has from 1 to 6 carbon atoms.
- 11) The process according to claim 10 wherein the primary alcohol is selected from methanol and/or ethanol.
- 12) The process according to claim 1 wherein the alkyl ether has from 5 to 10 carbon atoms.
- 13) The process according to claim 12 wherein the alkyl ether is selected from MTBE, ETBE, MSBE, ESBE or mixtures of these.
- 14) The process according to at least one of the previous claims comprising the following basic steps:
 - a) feeding to a dimerization reactor the hydrocarbon cut containing isobutene together with a stream consisting of primary alcohols and a stream containing alkyl ethers;
 - b) sending the product leaving the dimerization reactor to a fractionation column from whose head a stream is obtained containing non-reacted isobutene and small quantities of ethers and alcohols and from the bottom of which a stream containing dimers and alkyl ethers is removed;

- c) sending the stream containing the non-reacted isobutene to a second reactor to complete the conversion of isobutene;
- 3 d) sending the product leaving the second reactor to a second fractionation column from whose head a stream is obtained containing C_4 hydrocarbons and primary alcohols and from whose bottom a stream containing C_4 hydrocarbons, dimers and alkyl ethers is removed;
- 10 e) sending to a third fractionation column the bottom streams removed from the two fractionation columns obtaining the desired hydrocarbon product at the bottom and a stream containing alkyl ethers at the head, which is
- 15 recycled to the first reactor;
- f) sending the stream leaving the head of the second fractionation column to a separation unit of the primary alcohols which are subsequently recycled to the first reactor.



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Claims searched: 1-14

Examiner: Dr J Houlihan
Date of search: 21 July 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C5E (ECA, ECC, ECD, ECF, ECK), C5G (GAD)

Int Cl (Ed.6): C07C 2/14, C10G 50/00, C10L 1/02

Other: ONLINE: WPI, CLAIMS, JAPIO, TULSA

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0048893 A1 (EC ERDÖLCHEMIE GMBH) page 1 lines 1-5; Beispiel 2; & WPI Abstract Acc. No. 82-28939E/198215	1-13
X	US 4540839 (KEYWORTH D A & McFARLAND C G) column 2 lines 55-67; column 3 lines 15-17; Example 3; Claims 2 & 5	1-13

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.